

BIO-OIL PRODUCTION FROM PYROLYSIS OF PALM OIL WASTES

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ABSTRACT

Energy demand is increasing rapidly because of the growth of population and industrialization. However, the conventional energy source is depleting. Biomass is abundant but inefficiently utilized. Pyrolysis of biomass is the one of the alternative ways to encounter this problem. The products of pyrolysis are bio-oil, char and gas. In this research, the production of bio oil from the pyrolysis of palm oil fiber (POF) and palm oil empty fruit bunch (EFB) were studied using a small lab scale pyrolysis unit. The objectives of this research are to investigate the effect of sample size and produce bio oil from EFB and POF. Preliminary analysis was conducted using thermo gravimetric analyzer (TGA) to determine the volatility, ash residue and moisture content. From the result of the TGA, it is found that EFB contain more volatile matter in comparison to POF. It can also be concluded that EFB might produced more bio oil than POF. Meanwhile, the effect of sample size towards the yield was also studied. The sample size was varied between < 0.63 mm, 0.63-2 mm and 2-4 mm. The best size, which is < 0.63 mm, was pyrolysed in a reactor at constant temperature of 500 °C. The general characteristic of the product was investigated by the determination of functional groups present in bio oil using Fourier Transform Infrared spectrometer (FTIR). From the analysis, it is shown that bio oil contains complex compounds mostly functional groups of phenol, alcohol, ketones, aldehydes, carboxylic acid and carbonic structure. Physical properties of the bio oil such as pH and viscosity were also investigated. From the result, the pH for the bio oil is 3.99 and the viscosity value is 34 cP.

ABSTRAK

Permintaan tenaga semakin meningkat kerana pertumbuhan penduduk dan perindustrian. Walau bagaimanapun, sumber tenaga konvensional semakin berkurangan. Biojisim adalah banyak tetapi tidak cekap digunakan. Pirolisis biojisim adalah salah satu cara alternatif untuk menghadapi masalah ini. Produk pirolisis ialah minyak bio, arang dan gas. Dalam kajian ini, pengeluaran minyak bio daripada pirolisis gentian minyak sawit (POF) dan tandan buah kelapa sawit kosong (EFB) telah dikaji dengan menggunakan unit pirolisis makmal kecil. Objektif kajian ini adalah untuk mengkaji kesan saiz sampel dan menghasilkan minyak bio daripada EFB dan POF. Analisis awal telah dijalankan menggunakan termo gravimetrik Analisis (TGA) untuk menentukan bahan meruap, abu dan kandungan kelembapan. Daripada hasil daripada TGA, didapati bahawa EFB mengandungi bahan meruap lebih banyak berbanding dengan POF. Dapat disimpulkan bahawa EFB mungkin menghasilkan lebih banyak minyak bio daripada POF. Sementara itu, kesan saiz sampel ke arah hasil yang juga dikaji. Saiz sampel yang berbeza di antara < 0.63 mm, mm 0.63-2 dan 2-4 mm. Saiz terbaik iaitu < 0.63 mm menjalani proses pirolisis di dalam sebuah reaktor pada suhu malar sebanyak 500°C . Ciri-ciri umum produk telah disiasat oleh penentuan kumpulan berfungsi yang hadir dalam minyak bio menggunakan spektrometer inframerah transformasi Fourier (FTIR). Daripada analisis, ia telah menunjukkan bahawa minyak bio mengandungi sebatian kompleks kebanyakannya kumpulan fenol, alkohol, keton, aldehid, asid karboksilik dan struktur karbonik. Sifat fizikal minyak bio seperti pH dan kelikatan juga disiasat. Dari hasilnya, pH untuk minyak bio adalah 3.99 dan nilai kelikatan adalah 34 cP.

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LIST OF SYMBOLS

g	-	gram
min	-	minute
°C	-	degree Celsius
wt%	-	weight percentage
%	-	percentage
psi	-	unit of pressure
mm	-	millimeter
Mpa	-	Mega Pascal (unit of pressure)
s	-	second
CO ₂	-	carbon dioxide
H ₂ O	-	water
CO	-	carbon monoxide
CH ₄	-	methane
t _r	-	reaction time
KBr	-	potassium bromide

CHAPTER 1

INTRODUCTION

1.1 Research Background

Currently, the demand for energy is increasing rapidly due to the growth of population and industrialization. The world community have devoted their industries on coal and petroleum, which were plenty and cheap before the Middle East War in 1973. But with the oil crisis after the war, depletion of natural reserves of coal and oil has attracted great interest to sustainable energy production (Zheng, 2008). Since the fossil fuels reserves gradually deplete, renewable energy is now become very important (Jun et al., 2009). So, renewable energy source such as biomass play an important role in the production of energy. Compared with the use of fossil fuel, the use of biomass can reduce the emission of CO₂ which will cause to global warming and greenhouse effect (Jun et al., 2009).

Biomass is a renewable energy resource which can be changed into electricity and fuels by different processes such as combustion, gasification or pyrolysis. It is also refers to living and recently dead biological material that can be used as fuel or for industrial production. It is also include biodegradable wastes that can be burnt as fuel (Biomass, 2008). Other than that, biomass provides a clean energy that can improve environment. Biomass is grown from several plants included miscanthus, switchgrass, hemp, corn, poplar, willow, sugarcane, palm oil and many more. Biomass such as palm oil empty fruit bunches; fiber and shell are generated every year in Malaysia with an annual increment of 5% (Sukiran et al., 2009).

Malaysia, as the largest producer of palm oil in the world, generates a significant amount of palm oil wastes. Malaysia generates 7.7 million tones of empty fruit bunch (EFB), 6.0 million tones of fiber and 2.4 million tones of palm shell every year as wastes. The fiber wastes are used to produce energy by incinerating the waste for power and fertilizer purposes. Usually, palm oil mills have excess fiber and shell which have to be disposed off separately. There are more than 270 palm oil mills operating in Malaysia that utilize mainly fiber and partly shell in their boilers as fuel to generate power and steam required (Kawser and Nash, 2000).



Figure 1.1: Abundance of oil palm biomass (Ahmad et al., 2009)

Pyrolysis is one of the thermo chemical processes, which convert the biomass into liquid (bio- oil), gas and char. Biomass pyrolysis converts basically 80–95% of the feed material to gases and bio-oil. The pyrolysis process is to optimize the production of liquids which is including tar and bio-oil. The liquid products have high energy density, ease of transportation & storage and have the potential to be upgraded as fuels similar to refined premium-grade fuels (Williams & Bessler, 1996).

1.2 Problem Statement

Production of bio oil is quite challenging to engineering world today. It is a lot more challenging when it comes to the production of high yield of bio oil. In bio oil production, it is well known that biomass can be used to generate bio oil. According to Xu et al. (2011) grape residues, sugarcane residues, palm oil residues and forestry residue can be used as a sample for the pyrolysis processes. Most research has been performed on wood biomass because of its consistency and comparability between tests (Mohan et al., 2006). Palm oil wastes are high potential biomass energy sources that are CO₂ neutral. There is abundance of palm oil waste at Malaysia which is about 90%. Once the type of biomass has been considered, it is realized that another factor that also will contributing to the yield of bio oil is sample size.

1.3 Objective Of Research

The objectives of this research are:

- to investigate the effect of sample size and produce bio oil from Empty Fruit Bunch Fiber (EFB) and Palm Oil Fiber (POF).
- to determine the characterization of the bio oil.

1.4 Scope Of The Study

This research mainly focuses on:

1. parameters that have been evaluated in this study were sample size (< 0.63 mm, 0.63-2 mm, 2-4 mm) and type of biomass.
2. production of bio oil from biomass. Bio oil was obtained from palm oil wastes via pyrolysis at temperature 500°C.
3. characterized the bio oil that produced from palm oil wastes using Fourier Transform Infrared (FTIR).The pH and viscosity of the bio oil were also determined.

1.5 Rational And Significance

The EFB fiber and POF fiber was chosen to be compared between each other in order to determine which one of them contributes to high yield of bio oil. It is also decided that samples with range of < 0.63 mm, 0.63-2 mm and 2-4 mm size were compared to see how those factors lead to the production of high quality bio oil. This is based on size range suggested by Seebauer et al. (1997) studies. Sample size of 0.1mm to 2mm has been used in his study in order to determine the effect of sample size to the formation of bio oil.

The study of factors that influencing the production of high yield and quality of bio oil is very important to the community. Bio oil can replace fossil fuel that widely used now and known to be finished in less than 100 years from now. It can help s to solve the problems of shortage in supplies of fossil fuel by replacing it with a renewable energy source such as biomass. So, this study is crucial to help sustaining the energy supplies in the future for the sake of our next generations.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Concern over the global warming and fossil fuel reserves have led to the realization that a more environmentally friendly is required. Biofuels are seen have a good potential solution for this problem. Biofuels is a type of fuel whose energy is derived from biological carbon fixation. Biofuels include fuels derived from biomass conversion with solid biomass, liquid fuels and various biogases. Biofuels are gaining increased public and scientific attention because of factors such as oil price hikes, concern over greenhouse gas emissions from fossil fuels, and support from government subsidies. In 2010 worldwide biofuel production reached 105 billion liters and biofuels provided 2.7 % of the world's fuels for road transport, a contribution largely made up of ethanol and biodiesel (Biofuel, 2012). According to the International Energy Agency, biofuels have the potential to meet more than a quarter of world demand for transportation fuels by 2050.

2.2 Biomass

Biomass is the word used for all organic material originating from plants, trees and crops and is essentially the collection and storage of the sun's energy through photosynthesis. Biomass energy is the change of biomass into valuable forms of energy such as heat, electricity and fuels. It comes either directly from the land or from residues generated in the processing of crops for food or other products such as pulp and paper from the wood industry. The biomass to bioenergy system can be considered as the management of flow of solar generated materials, food, and fiber in society. These interrelationships are shown in Figure 2.1, which presents the various resource types and applications, showing the flow of their harvest and residues to bioenergy applications.

Not all biomass is directly used to produce energy but rather it can be converted into intermediate energy carriers called biofuels. This includes charcoal (higher energy density solid fuel), ethanol (liquid fuel) or producer-gas (from gasification of biomass) (Antonia et al., 2000).

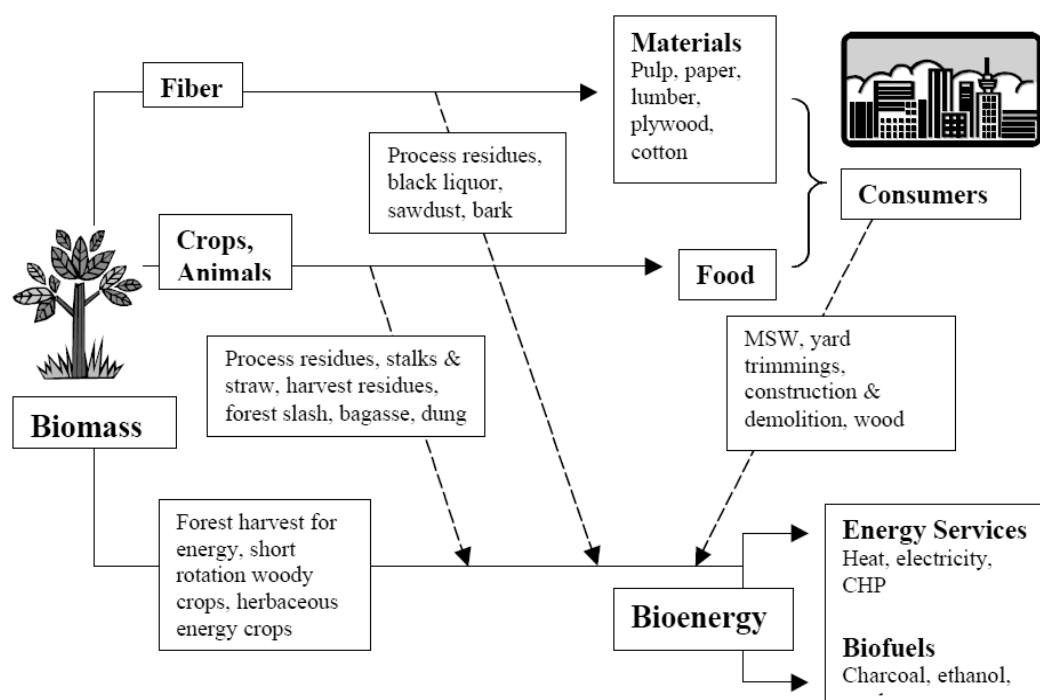


Figure 2.1: Biomass and Bioenergy flowchart (Antonia et al., 2000)

2.3 Type of Biomass

Biomass comes from a variety of sources as shown in table 2.1

Group Biomass	Subclassifications	Examples
Virgin	Terrestrial biomass	Forest biomass
		Grasses
		Energy crops
	Aquatic biomass	Cultivated crops
		Algae
Waste	Municipal waste	Water plant
		Municipal solid waste
	Agricultural solid waste	Biosolids, sewage
		Landfill gas
		Livestock and manures
	Forestry residues	Agricultural crop residue
		Bark, leaves, floor residues
	Industrial wastes	Demolition wood, sawdust
Waste oil or fat		

Table 2.1: Two major groups of biomass and their sub classifications (Basu, 2010)

Virgin biomass comes directly from plant and animals which include wood, plants, leaves, crops and vegetables. Waste includes solid and liquid waste, sewage, animal and human waste, gases derived from land filling and agricultural wastes (Basu, 2010).

2.4 Resource of biomass

Biomass can be obtained from different sources such as wastes, standing forest and energy crops. The wastes categories comprise waste from agricultural production, process waste from agro industries, crop residues and many more. Standing forest consist of different intermediate products and residuals wastes of different nature. An

energy crop includes various edible and non-edible crops (Saxena et al., 2009). Biomass resources can be categorized into modern biomass and traditional biomass. Modern biomass involves large scale uses and use to substitute for conventional energy sources. Meanwhile traditional biomass involves small scale uses and use to developing countries.

2.5 Biomass utilization

Biomass has always been a main source of energy for mankind from early. Currently, it contributes around 10–14 % of the world's energy supply (Putun, et al., 2001). Biomass can be converted into three main types of products:

- Electrical or heat energy.
- Fuel for transport sector.
- Feedstock for chemicals.

Conventionally, biomass had been utilized through direct combustion. Pollutants with dust and the acid rain gases such as sulfur dioxide and nitrogen oxides will produce when the biomass is burned. But, the sulfur dioxide produced is 90 % less than that is produced by burning coal (Saxena et al., 2009). The quantities of atmospheric pollution produced are insignificant compared to other pollution sources. Biomass usage as a source of energy is of interest due to the following envisaged benefits:

- Biomass is a renewable, potentially sustainable and environmentally friendly source of energy.
- A gigantic range of diverse materials, frequently stereo chemically defined, are available from the biomass giving the user many new structural features to develop (Joseph, 1999).
- The increased use of biomass would avoid diminishing crude oil supplies.
- Biomass fuels have small sulfur content and the amount will not contribute to sulfur dioxide emissions that cause acid rain.

- The combustion of biomass produces less ash than coal combustion and the ash produced can be used as a soil additive on farms and many more.
- The combustion of agricultural, forestry residues and municipal solid wastes (MSW) for energy production is an effective use of waste products that reduces the significant problem of waste disposal.
- Biomass provides a clean, renewable energy source that could improve our environment, economy and energy securities (Othmer, 1980).
- Biomass usage could be a way to prevent more carbon dioxide production in the atmosphere.

Biomass can be used in several ways to obtain energy. Most of the biomass energy is consumed in domestic purposes and by wood-related industries. It is burned by direct combustion to produce steam that drives the turbine or generator to produce electricity. Gasifiers are used to convert biomass into a combustible gas which is then used to drive a high efficiency, combined cycle gas turbine. Biomass is converted to pyrolysis oil by heating. Pyrolysis oil is easier to store and transport than solid biomass material and is burned like petroleum to generate electricity (Saxena et al., 2009).

2.6 Biomass components

The significance of particular type of biomass depends on the chemical and physical properties of the large molecules from which it is made. The chemical structure and major organic components in biomass are important in the development of processes for producing fuel and chemicals. Biomass contains varying amounts of cellulose, hemicellulose, lignin and a little of extractive (Bridgewater, 1999). Cellulose is a glucose polymer containing linear chains of (1, 4)-D-glucopyranose units, in which the units are linked 1–4 in the alpha configuration, with an average molecular weight of around 100,000 (Saxena et al., 2009). Alpha cellulose is a polysaccharide having the general formulae ($C_6H_{10}O_5$). Hemicelluloses are complex polysaccharides that are present in association with cellulose in the cell wall. It is a mixture of polysaccharides, composed almost entirely of sugars such as glucose, mannose, xylose and arabinose and methylglucuronic and galaturonic acids (Saxena et al., 2009). Lignins are highly branched, substituted, mononuclear aromatic polymers in the cell walls of the certain

biomass and are often adjacent to cellulose fibers to form a lignocellulosic complex (Ana-Rita & Ian, 1996). In biomass, cellulose is generally the largest fraction, about 40–50 % by weight and hemicellulose about 20–40 % (McKendry, 2002).

2.7 Biomass conversion

The bulky of biomass is a major difficulty to a rapid shift from fossil to fuels. Biomass is hard to handle, transported and stored. So, this problem gives an idea for the conversion of solid biomass into liquid and gaseous fuel. The biomass conversion can be achieved through biochemical route and thermochemical route as shown in Figure 2.2 below.

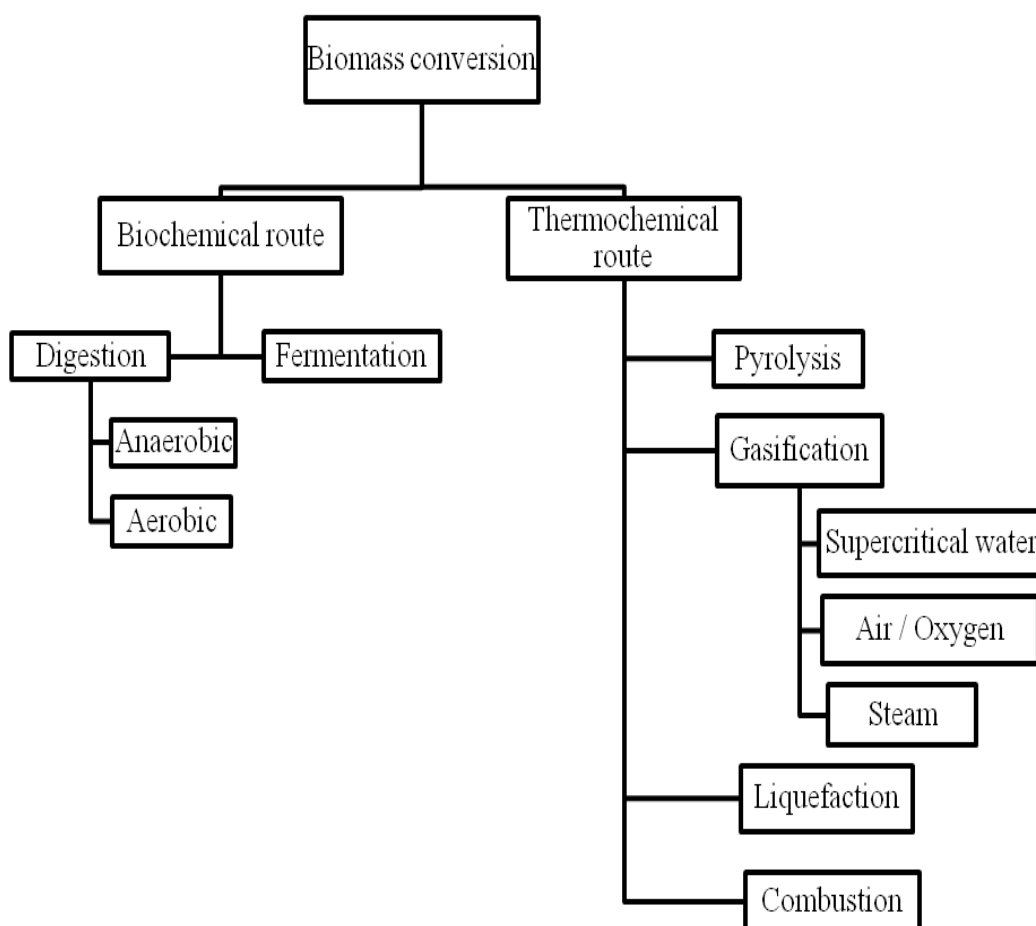


Figure 2.2: Biomass conversion (Basu, 2010)

2.8 Thermochemical conversion

Biomass is converted into gases in thermochemical conversion. The gases are then synthesized into the desired chemicals or used directly as shown in Figure 2.3 below. There are four main processes in thermochemical conversion which are combustion, gasification, liquefaction and pyrolysis.

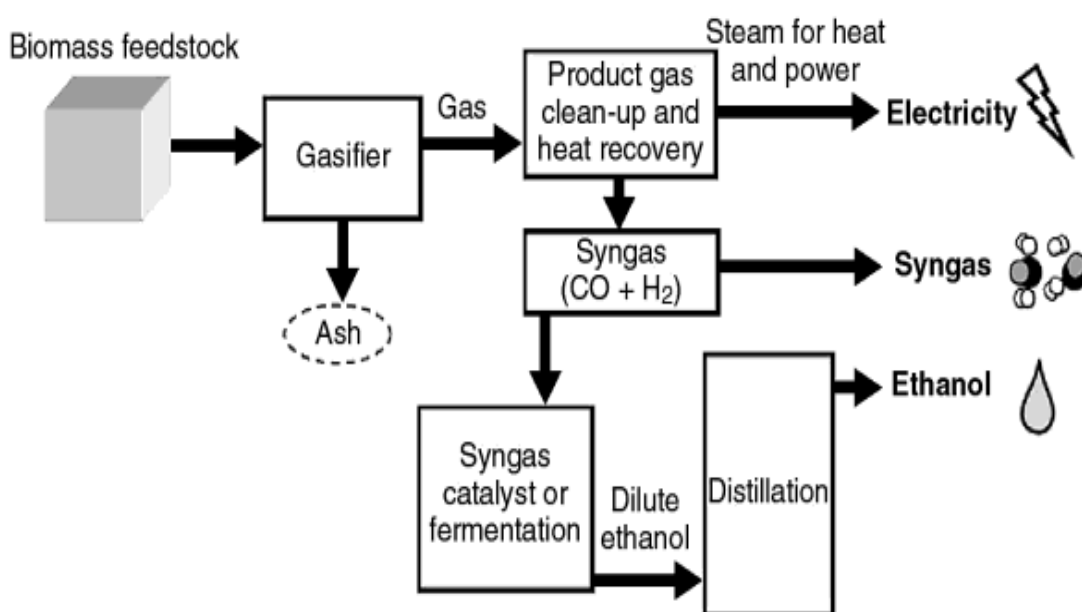


Figure 2.3: Thermochemical route for production of energy, gas and ethanol (Basu, 2010)

Combustion involves high temperature conversion of biomass in excess air. The products of combustion are carbon dioxide and water. Gasification involves a chemical reaction in insufficient oxygen environment. Pyrolysis takes place in the total absence of oxygen. For liquefaction, the large feedstock molecules are decomposed into liquids having smaller molecules.

Process	Temperature (°C)	Pressure (Mpa)	Catalyst	Drying
Liquefaction	250 – 330	5 – 20	Essential	Not required
Pyrolysis	380 – 530	0.1 – 0.5	Not required	Necessary
Combustion	700 – 1400	> 0.1	Not required	Not essential
Gasification	500 – 1300	> 0.1	Not Essential	Necessary

Table 2.2: Comparison of four main thermochemical conversion processes (Demirbas, 2009)

2.8.1 Combustion

Combustion is the oldest utilization of biomass. Combustion is an exothermic reaction between oxygen and hydrocarbon of the biomass (Basu, 2010). The biomass will be converted into two major compounds which are H₂O and CO₂. Heat and electricity are two principal forms of energy obtained from biomass. Biomass provides heat for cooking and warmth especially in countryside areas. Industrial heating is also produced by steam generated in biomass fired boilers. Pellet stoves or log fired fireplaces is also a direct source of warmth in many cold weather country. Electricity, the foundation of all modern economic activities may be generated using from biomass combustion. The most ordinary practice involves the generation of steam by burning biomass in a boiler and the generation of electricity through a steam turbine. In some places, electricity is produced by burning combustible gas derived from biomass through gasification.

2.8.2 Gasification

Biomass gasification is a process that converts carbonaceous biomass into combustible gases such as H₂, CO, CO₂ and CH₄. It requires gas or supercritical water as a medium for reaction. Gaseous medium can be air, oxygen, subcritical steam or its mixture. For production of synthetic gases, gasification of fossil fuels is more common than non fossil fuels such as biomass. Gasification is important because of to increase

the heating value of the fuel by rejecting noncombustible components like nitrogen and water, to remove sulfur and nitrogen to avoid burnt nitrogen and sulfur from released to the atmosphere and to reduce the carbon to hydrogen (C/H) mass ratio in the fuel.

The higher the hydrogen contain in a fuel, the lower vaporization temperature (Basu, 2010). So, the probability of the fuel being in a gaseous state is higher. Gasification increases the relative hydrogen content (H/C ratio) in the product through direct, indirect and pyrolysis.

- Direct: Direct exposure to hydrogen at high pressure
- Indirect: Exposure to steam at high pressure and temperature where hydrogen as an intermediate product is added to the product. This process also includes steam reforming.
- Pyrolysis: Reduction of carbon by rejecting it through solid char or CO₂ gas (Basu, 2010).

Biomass provides two important benefits that make it a possible feedstock for syngas production. They are not make any net contribution to the atmosphere when burnt and it use reduces dependence on nonrenewable and often imported fossil fuel. Biomass gasification into CO and H₂ provides a good base for production of liquid transportation such as gasoline and methanol. Gasification is generally carried out in moving bed, fluidized bed and entrained flow. Downdraft and updraft are two common types of moving bed gasifier. Downdraft gasifier is the most common use in Europe, United Stat and Canada which is 75 % uses (Knoef, 2000).

2.8.3 Liquefaction

Liquefaction of solid biomass into liquid fuel can be done through pyrolysis, gasification and hydrothermal process. In the liquefaction, feedstock macromolecule compounds are decomposed into fragments of light molecules in the presence of a suitable catalyst. Direct liquefaction of wood by catalyst was carried out in the presence of K₂CO₃ (Ogi et al., 1985). The heavy oil obtained from the liquefaction process was a viscous tarry lump and sometimes caused problems during handling. So, some organic

solvents were added to the reaction system. Among the organic solvents tested, propanol, butanol, acetone, methyl ethyl ketone, and ethyl acetate were found to be effective on the formation of heavy oil having low viscosity (Demirbas, 2000).

2.9 Pyrolysis

Pyrolysis is one of the most promising thermo chemical conversion routes to recover energy from biomass. Pyrolysis is the process heating biomass in the absence of air and oxygen. The initial product of pyrolysis is made of condensable gases and solid char. The condensable gas may break down further into non condensable gases such as CO, CO₂, H₂ and CH₄, liquid and char. The yields of end products of pyrolysis and the composition of gases are dependent on the several parameters including temperature, biomass species, particle size, heating rate, operating pressure and reactor configuration.

Pyrolysis is a thermal degradation of the organic matrix in absence of oxygen to obtain an array of solid, liquid and gas (Serdar yarman, 2003). Pyrolysis utilized heat either directly or indirectly in order to decompose waste material. Pyrolysis is usually endothermic reaction and also occurs at high temperatures.

2.9.1 Types of Pyrolysis

Pyrolysis may be classified as slow and fast based on heating rate. For the slow pyrolysis, the time heating (t_{heating}) required to heat the fuel to the pyrolysis temperature is much longer than the characteristic pyrolysis reaction time (t_r). Usually, slow and fast pyrolysis are carried out in the absence of medium. Meanwhile, for the hydrous pyrolysis and hydrolysis both carried out in the medium. Hydrous pyrolysis carried out in H₂O while hydrolysis carried out in the H₂. These two types are mainly for the production of chemical.

In slow pyrolysis, the residence time of vapor in the pyrolysis zone is on the order of minutes or longer. Usually this process is used for char production and is broken down into carbonization and conventional. But, in fast pyrolysis the vapor residence time is on the order of seconds or milliseconds. Primarily this type of pyrolysis is for the production of bio oil.